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(54) PROCESS FOR FORMING A PROTECTIVE COATING ON FERROUS ARTICLES

(71) We, CRANE LIMITED, a British Company, of 15-16 Red Lion Court, Fleet Street, London, E.C.4, do hereby declare this invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement :—

This invention relates to a process for forming a protective coating on cast ferrous articles.

An article fabricated of ferrous metal has a strong propensity to corrode unless the metal is extensively alloyed with a non-ferrous metal such as chromium, for example, or the article is provided with a protective coating. An article made of cast or wrought iron, as well as a plain carbon steel, will readily corrode in an atmosphere where oxygen is present unless a protective coating is formed on the surface of the article. Since the use of a "stainless" steel, for example, in numerous applications where requirements dictate fabrication of an article in iron or steel, is prohibitively expensive, numerous coating and other surface protection methods have been developed.

The most commonly used simple coating for metal articles is paint. Another coating widely used on ferrous metal articles is zinc; i.e. galvanizing. Chromium plating is also employed where a hard and attractive surface is desirable.

Each of the above-mentioned methods necessarily requires performing a separate step after fabrication of the articles. This adds to production costs. Where a metallic coating such as chromium, for example, is applied, the increased cost factor is substantial. On the other hand, whereas a paint coating is considerably less expensive, it is also unsuitable in numerous applications of the ferrous article because the article is employed in an environment where the paint itself is attacked and readily breached.

[Price 25p]

In contrast to the known processes where a protective coating is provided after the metal article is fabricated, methods have been developed for forming an alloy-type coating on the cast metal during the casting operation. A process of this nature is described in United States Patent No. 1,725-039, where a chromium alloy surface is formed on a ferrous article by coating the mould surface with a chromium powder and an oxide formation inhibitor in an organic binder. The metallic chromium alloys with the molten base metal at the surface of the cast article.

In a broadly similar process, a hard surface coating of tungsten or molybedenum carbide is formed on a cast base metal by painting the mould cavity with the finely powdered coating material in a binder. The carbide coating formed on the surface of the base metal is highly resistant to wear and certain types of corrosion. This process is disclosed in United States Patent No. 1,981,403.

These two surface coating processes offer distinct advantages in the formation of protective surfaces on base metal castings in that the protective coatings are formed during the casting operation. There are other coating or surface treatment processes of this general nature, of course. None provides the ultimate simplicity and minimum cost factors which are highly desirable and constantly sought, however.

The present invention is directed to an improved, simple and inexpensive process for forming a hard, durable, corrosion-resistant coating on ferrous articles. More particularly, it relates to the development of a corrosion resistant surface on cast ferrous articles.

According to the invention, a process for producing a ferrous metal casting having on at least a portion of its surface a coating including a complex metal oxide as herein

defined possessing the properties of hardness durability and resistance to corrosion comprises the steps of providing a porous mould, applying to the part of the mould surface corresponding to the said portion of the casting surface a wash containing at least one metal oxide, or compound containing a metal oxide radical, which is capable of combining with an oxide of the metal to be cast to form the said complex oxide, drying the mould, and pouring molten ferrous metal into the mould whereby the oxygen present in the mould reacts with the cast metal to produce an oxide thereof over the whole surface of the casting and the metal oxide in the wash enters into the reaction over the said portion of the casting surface to form the complex oxide.

Preferably the compound used in the process comprises sodium chromate, sodium aluminate, aluminium oxide hydrate or hydroxide, or a rare earth metal oxide hydrate or hydroxide. This is applied to the surface of the mould in the form of a wash, i.e. by painting or daubing it onto the mould surface, the wash being a suspension or solution of the compound in a liquid.

The mould might be formed as a green sand mould, which is porous, or a chill mould, for example. The mould might be baked to a dry sand mould subsequent to the wash being applied, or the wash might be applied directly to a dry sand mould.

A molten ferrous base metal is introduced to the treated (painted or daubed) mould. As the base metal solidifies in the mould, the presence of free oxygen at the interface between the article and the mould causes oxidation to take place. Without prior treatment of the mould according to the invention, this oxidation would normally result in the formation of the base metal oxide on the article surface.

The normally formed base metal oxide would, of course, offer some resistance to corrosion. However, it is not a hard, durable surface which is highly resistant to corrosion in high temperature and pressure environments.

In the present invention, a more complex oxide is formed from both the base metal and the metallic element(s) in the compound(s) washed onto the surface of the mould prior to casting. One form of complex oxide produced by the invention is of the spinel type. The spinels are generally defined as a group of isomorphous mineral oxides having the generic formula AB_2O_4 where A is one of a group of metals including ferrous iron, zinc and magnesium, and B is one of a group of metals including aluminium, ferric iron and chromium. The spinel type complex oxides are characterized by their gem-like hardness and extremely high resistance to corrosion.

However, the complex oxides with which the invention is concerned are not confined to the spinels. For example, if the oxides of two metals of group A referred to above and one metal of group B were present it would be possible for two different types of spinel to be formed, but in practice a complex oxide of the three metals results. Similarly it is possible to form a complex oxide of more than three metals. The complex oxides with which the invention is concerned all have the common feature that they produce a coating which has the characteristic gem-like hardness and appearance, and the high corrosion resistance which is characteristic of the spinel.

The coatings referred to, because of their hardness and durability, are highly corrosion resistant under extremely adverse conditions, including those aforementioned conditions where high temperatures and pressures are encountered and corrosion is normally a serious problem.

The use and application of the process embodying features of the invention may best be understood by an example. A boiler casting is necessarily exposed to the corrosive and erosive action of fluids under high pressures and temperatures on its inner surfaces. Because of the economic facts involved in providing a corrosion resistant coating on the exposed inner surface of such a casting by conventional and well-known techniques, it is customary in boiler castings to rely on the oxide coating normally formed on the surface during casting as a corrosion inhibitor. Unfortunately, although this oxide coating does provide a certain deterrent factor, corrosion still occurs at a rapid rate because of the nature of the environment.

To make the inner surface of the boiler casting highly corrosion resistant according to the present invention, a wash is prepared comprising a solution of sodium chromate (Na_2CrO_4), for example, in water. At the same time, conventional green sand mould, for example, is prepared. The wash is painted or daubed on the surface of the mould core where a corrosion resistant surface is desired on the article being cast. The green sand mould is then baked at approximately 400°F - 600°F to form a dry sand mould with the sodium chromate present on the mould core surfaces which have been treated with the wash.

The mould having been prepared in the aforedescribed manner, molten iron is introduced into the mould by conventional techniques. The molten iron solidifies in the mould to form the article being cast; in the present instance a boiler casting. The normal presence of oxygen in the sand at the interface between the hot, solidifying article and the mould surface causes oxida-

tion of the casting base metal to take place on the casting surface.

In the present invention this oxidation process is more complex than merely a formation of base metal oxide. As the iron oxidizes, the chromium in the sodium chromate enters into the oxidation reaction. A complex oxide of the spinel type is thermally formed on the surface of the article by the oxidation process.

The spinel-type oxide complex which forms on the surface of the cast ferrous article has, in a characteristic manner, a gem-like hard surface. This surface is extremely durable and corrosion resistant under the substantially adverse conditions to which a boiler casting inner surface is subjected; i.e. high pressures and temperatures.

In the example utilized, the "mould" has been described as a green sand mould which is baked to a dry sand mould prior to casting an after the "wash" is applied. It should be reiterated here that the invention also contemplates applying the wash to a chill mould, for example, or a dry sand mould after baking. It is further within the purview of the invention that the wash be appplied and the invention employed with various other types of moulds.

In addition, the exemplary wash employed is an aqueous solution of sodium chromate. The wash might, however, comprise a sodium aluminate, aluminium oxide hydrate, or rare earth metal oxide hydrate compound in aqueous solution. In any such case a hard, durable, corrosion resistant surface of the nature contemplated is formed.

The corrosion resistant surface which is formed on the surface of a cast metal article such as a boiler casting or the like by the process embodying features of the invention is highly effective under the most adverse conditions. Nevertheless, the process itself is exceedingly simple and inexpensive. Cast ferrous articles can be made with highly corrosion resistant surfaces at costs compatible with their applications.

WHAT WE CLAIM IS :—

1. A process for producing a ferrous metal casting having on at least a portion of its surface a coating including a complex metal oxide as herein defined possessing the properties of hardness durability and resistance to corrosion comprising the steps of providing a porous mould, applying to the part of the mould surface corresponding to the said portion of the casting surface a wash containing at least one metal oxide, or compound containing a metal oxide radical, which is capable of combining with an oxide of the metal to be cast to form the said complex oxide, drying the mould, and pouring molten ferrous metal into the mould whereby the oxygen present in the mould reacts with the cast metal to produce an oxide thereof over the whole surface of the casting and the metal oxide in the wash enters into the reaction over the said portion of the casting surface to form the complex oxide.

2. A process according to claim 1, wherein the compound contains a metal oxide of the kind which, in combination with the oxide of the cast metal, forms a complex oxide of the spinel type as herein defined.

3. A process according to claim 1 or 2, wherein the compound is sodium chromate, sodium aluminate, aluminium oxide hydrate or hydroxide, or a rare earth metal oxide hydrate or hydroxide.

4. A process according to any preceding claim, wherein the compound is applied as a suspension or solution in a liquid.

5. A process according to claim 4, wherein the liquid is water.

6. A process according to any preceding claim, wherein the mould is a sand mould.

7. A process according to claim 6, wherein the mould is a green sand mould which is baked after the application of the compound to form a dry sand mould.

8. A process according to claim 1 substantially as described herein by way of example.

9. A ferrous casting having a hard, durable and corrosion-resistant coating produced by a proces according to any one of claims 1-8.

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